

Activated Carbon

for Bromate Reduction

Activated carbon is well-known for its ability to remove organic compounds from water through a process known as adsorption, remove chlorine and chloramine through various chemical reactions, and serve as a general filter medium. However, its use for reduction of bromate is unclear. Various authors have studied the use of activated carbon and for the most part have concluded activated carbon is not a cost-effective solution. However, these authors have failed to realize the limitations of carbon validation methods or the fact that

not all carbons are alike, especially when chemical reactions control the process.

Regulations and Reactions

Bromate (BrO_3^-) is a disinfection byproduct formed by the reaction of ozone and naturally occurring bromine in drinking water. Although bromate is unlikely to be formed using standard chlorination disinfection, there is some evidence that commercially available sodium

hypochlorite solutions may contain bromate as a contaminant.¹ Bromate is a highly toxic substance that causes irreversible renal failure, deafness and death and has been linked to renal tumors in rats. As such, the American, Canadian and European environmental protection agencies have designated 10 $\mu\text{g/L}$ as the maximum acceptable concentration or maximum contaminant level (MCL) in drinking water.

The important precursor to bromate formation in drinking water is bromide. In the United States, the average bromide concentration in drinking water is approximately 100 $\mu\text{g/L}$. Since bromate is 63 percent bromide, only 6.3 $\mu\text{g/L}$ of bromide needs to be converted to bromate upon ozonation to exceed the MCL. Natural sources of bromine in groundwater are saltwater intrusion and bromide dissolution from sedimentary rocks. Bromine usually is present in drinking water as either hypobromous acid (HOBr) or hypobromite (OBr^-). When exposed to ozonation, the bromide ion

readily is oxidized to aqueous bromine. In addition to bromate, aqueous bromine can cause various types of brominated disinfection byproducts such as bromoform and brominated haloacetic acids.

In order to understand the formation of aqueous bromate, a corollary understanding of ozone decomposition is needed. Ozone can play a direct (molecular ozone pathway) or indirect (hydroxyl radical pathway) oxidative role in forming byproducts. Ozone reacts directly with the bromide ion to form hypobromite and oxygen.



Two ozone molecules then react directly with the hypobromite to form bromate and oxygen. Alternatively, the hypobromite can react with multiple hydroxyl radicals created by the destruction of ozone.



These reactions are generalized and not necessarily balanced, but they give a good overview of the mechanisms at work in bromate formation.

While the 10 $\mu\text{g/L}$ MCL is anticipated to impact a limited number of utilities currently using ozone as the primary disinfectant to inactivate *Giardia* and viruses, a greater number of utilities will be impacted by this MCL when compliance with the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) is required. Compliance will mean continuance of meeting filtration avoidance criteria of two-log *Cryptosporidium* inactivation and overall inactivation requirements (three-log *Giardia*, four-log viruses and two-log *Cryptosporidium*) using a minimum of two disinfectants.

Activated Carbon Research for Bromate Reduction

The use of activated carbon has been investigated by various authors for the removal or reduction of bromate.^{2,3,4} The data to date have been inconsistent and, in some cases, misleading due to the techniques used to determine the applicability of activated carbon.^{5,6} It also is apparent

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Table 1. Carbon Properties

Test Procedure	Catalytically Enhanced GAC (8x30 mesh)	Standard Bituminous GAC (8x30 mesh)
Mean Particle Diameter (mm) (Used for Testing)	1.44	1.44
Peroxide Number (Used for Testing)	6.6	53.0
Iodine Number (Specification)	825 minimum	900 minimum

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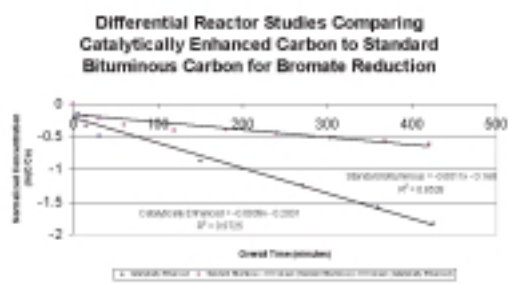
Standard Ozone System #2:
Eliminates up to 5 ppm iron & manganese, 5 ppm sulfur, & up to 12 gpm.

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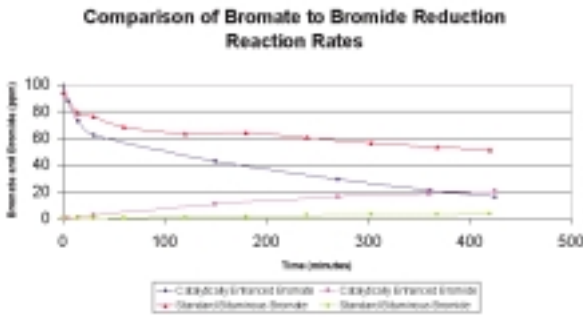
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Figure 1



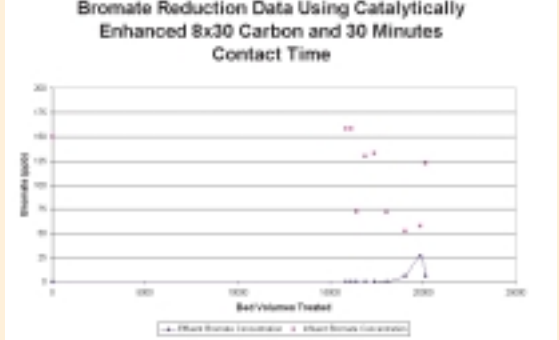
Reaction Rate Data Comparing Catalytically Enhanced GAC to Standard Bituminous GAC

Figure 2



Bromate Reduction and Bromide Formation Data

Figure 3



Column Study Data

that the carbon selection process was overlooked, which has led to generalizations concerning the use of activated carbon for this application.

One paper however has focused on the effect of surface properties on bromate removal.⁷ The data shows surface properties can and do affect bromate removal performance. Other applications such as chloramine removal in the liquid phase and hydrogen sulfide and sulfur dioxide oxidation in the vapor phase also have been shown to be affected by surface properties. Commercially available activated carbons produced for catalytic properties as well as adsorptive properties do exist and have been investigated for bromate reduction. However, the data is misleading due to testing conditions.

Activated Carbon for Bromate Reduction—Reaction Kinetics

Testing was conducted using a differential reactor to determine the reaction rate for a standard bituminous coal-based granular carbon and a catalytically enhanced carbon. Typical carbon properties are shown in Table 1. Reaction rate data (Figure 1) show the reaction follows a first order reaction and, more importantly, data show the reaction rate for the catalytically enhanced carbon is 3.4 times faster than the standard carbon.

Analysis of the water confirms the reaction product from bromate destruction is bromide (Figure 2). The faster reaction rate for the catalytically enhanced carbon would allow shorter contact time systems to be designed for full-scale use. Experimental design

studies show typical properties such as iodine number cannot be used to predict bromate reduction performance, however, catalytic activity as measured by the peroxide number is useful in determining the more applicable carbon.

Activated Carbon—Real World Application

Differential reactor studies are useful for the determination of reaction rates. However, full scale testing is required to verify the data. Studies published concerning the reduction of bromate have utilized the Rapid Small Scale Column Test (RSSCT) procedure, which was designed for adsorption applications and may not translate well to applications where a different removal mechanism such as oxidation/reduction or ion exchange exists. Data from the literature as well as the differential reactor work conducted for this paper show the reaction to be a reduction of bromate; therefore, the RSSCT column study procedure may not be accurate.

Column studies were conducted using actual particle size carbons and full-scale contact times to verify performance. A column study using a 30-minute contact time and catalytically enhanced 8x30 mesh carbon showed bromate could be successfully reduced from an average of 110 ppb bromate to an average of less than 5 ppb (see Figure 3).

Conclusions

- Differential reactor studies indicate the bromate reduction reaction to bromide to be first order.

- Data show standard carbon properties such as iodine number cannot be used to indicate bromate reduction performance.
- Catalytic activity as measured by the peroxide number does give some indication of bromate reduction performance.
- Column study data show activated carbon can be utilized to reduce bromate to acceptable levels. **WQP**

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